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CESIUM PACKAGING STUDIES
CONVERSION OF CESIUM ZINC FERROCYANIDE
TO A CESIUM CHLORIDE PRODUCT

By

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and

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I. INTRODUCTION

There has been continuing interest at Hanford in the recovery of fission products from plant wastes and their use as radiation sources.[1] The principal fission product for these purposes is thought to be cesium-137, which has a half life of thirty years with beta energies of 0.52 and 1.18 Mev and a gamma energy (barium-137 daughter) of 0.662 Mev.

As early as 1953, work had been done on the recovery of cesium from Purex waste streams. Both R. E. Burns, et al.[2] and E. A. Coppinger[3] presented flowsheets describing the recovery of cesium with ferrocyanides, which included calcination processes. Extensive investigations on calcination processes have also been reported at Arco, Idaho.[4] H. H. Van Tuyl[5,6,7] has recently developed a process for recovering cesium from Purex plant wastes using metal ferrocyanides, of which cesium zinc ferrocyanide was considered the best for neutralized waste solutions. Nickel and ferric ferrocyanides were also found to be effective in acid solutions.

Although cesium zinc ferrocyanide is chemically stable and nearly one-half cesium by weight, two important characteristics desired in a radiation source, there is some fear that ferrocyanides undergo slow radiation decomposition with rupture of the CN bond and resultant pressure build-up. Therefore, an investigation was carried out to develop methods for the conversion of metal ferrocyanides to a radiation stable compound. A second important reason for this investigation was a desire for a higher specific activity than is afforded with cesium zinc ferrocyanide (theoretically 59.5 curies/cc). At Oak Ridge National Laboratory,[8] it has been found that cesium chloride is stable to its own radiation and is, therefore, a suitable radiation source.

The present work was undertaken with the objective of developing processes for the conversion of cesium zinc ferrocyanide to cesium chloride, or cesium chloride containing material. Both "wet chemistry" and "dry chemistry" techniques were investigated.

II. SUMMARY

1. The composition of cesium zinc ferrocyanide was found to be

$$Cs_2ZnFe(CN)_6$$
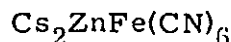
with one to two waters of hydration, depending on the temperature of drying. The crystal structure is isomorphous with potassium zinc ferrocyanide, being face centered cubic with a cell parameter of 10.2 $\overset{o}{A}$ and a calculated crystallographic density of about 3.44 gms/cc.

2. It appears that some radiation decomposition occurs when cesium zinc ferrocyanide is exposed to gamma radiation from cobalt-60 or to 1.9 Mev electrons from a Van de Graaff electrostatic accelerator; however, there is some uncertainty regarding the exact extent of degradation which would result from self-irradiation.

3. A process for the conversion of cesium zinc ferrocyanide to a product containing cesium chloride was developed. The process employs a calcination-chlorination step to convert the cations to chlorides and oxides. The final product was found to be

$$2CsCl \cdot ZnCl_2 + 1/2\ Fe_2O_3.$$
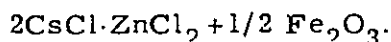
A flowsheet is shown describing this process.

Explosions were sometimes observed when cesium zinc ferrocyanide was heated, but two washes with water were sufficient to remove the sodium nitrate which caused the explosions.

4. A second "dry chemistry" process was developed to convert cesium zinc ferrocyanide to a pure cesium chloride product. This process employed a calcination followed by water leaching, acidification with hydrochloric acid, and evaporation to dryness. A flowsheet is appended.

<div align="right">UNCLASSIFIED</div>

5. A "wet chemistry" process was developed wherein cesium zinc ferrocyanide is dissolved with hot concentrated sulfuric acid followed by subsequent removal of undesirable ions by sulfide precipitation and anion exchange. The final product again is cesium chloride. A flowsheet is shown describing the process.

6. An alternate "wet chemistry" process is described using a mercury cathode cell for the reduction and removal of undesirable cations. A flowsheet is shown with cesium chloride as the final product.

7. All except the calcination-leaching process were found to be equally applicable to cesium-containing nickel ferrocyanide, ferric ferrocyanide, or zinc ferricyanide precipitates.

III. EXPERIMENTAL

The cesium zinc ferrocyanide used in this investigation was prepared by combining solutions of cesium and zinc nitrates with potassium ferro-cyanide in stoichiometric ratio to form $Cs_2ZnFe(CN)_6$. Radiocesium-137 obtained from Oak Ridge was spiked in to trace the cesium in the various processes used. When nickel or iron was used instead of zinc, three-fold excesses of ferrocyanide and iron or nickel were used to simulate the same degree of cesium scavenging. In the calcination or calcination-chlorination experiments, the cesium zinc ferrocyanide precipitate was washed three times in dis'illed water and once in ethyl alcohol, dried in an oven at 10C C for four hours, and then pulverized. The powder was then placed in a porcelain boat and weighed. The boat was inserted into a pyrex furnace tube in an electric tube furnace. Air, oxygen, or a mixture of air and chlorine was passed over the boat containing the compound, and the tempera-ture was increased slowly over a four hour period to the desired temperature and held constant at that temperature for another two to four hour period. During this latter time the chlorine gas was shut off in the calcination-chlorination process.

In the wet chemical process, the precipitate was washed three times in water and dissolved with hot concentrated sulfuric acid and treated as shown in another section of this report.
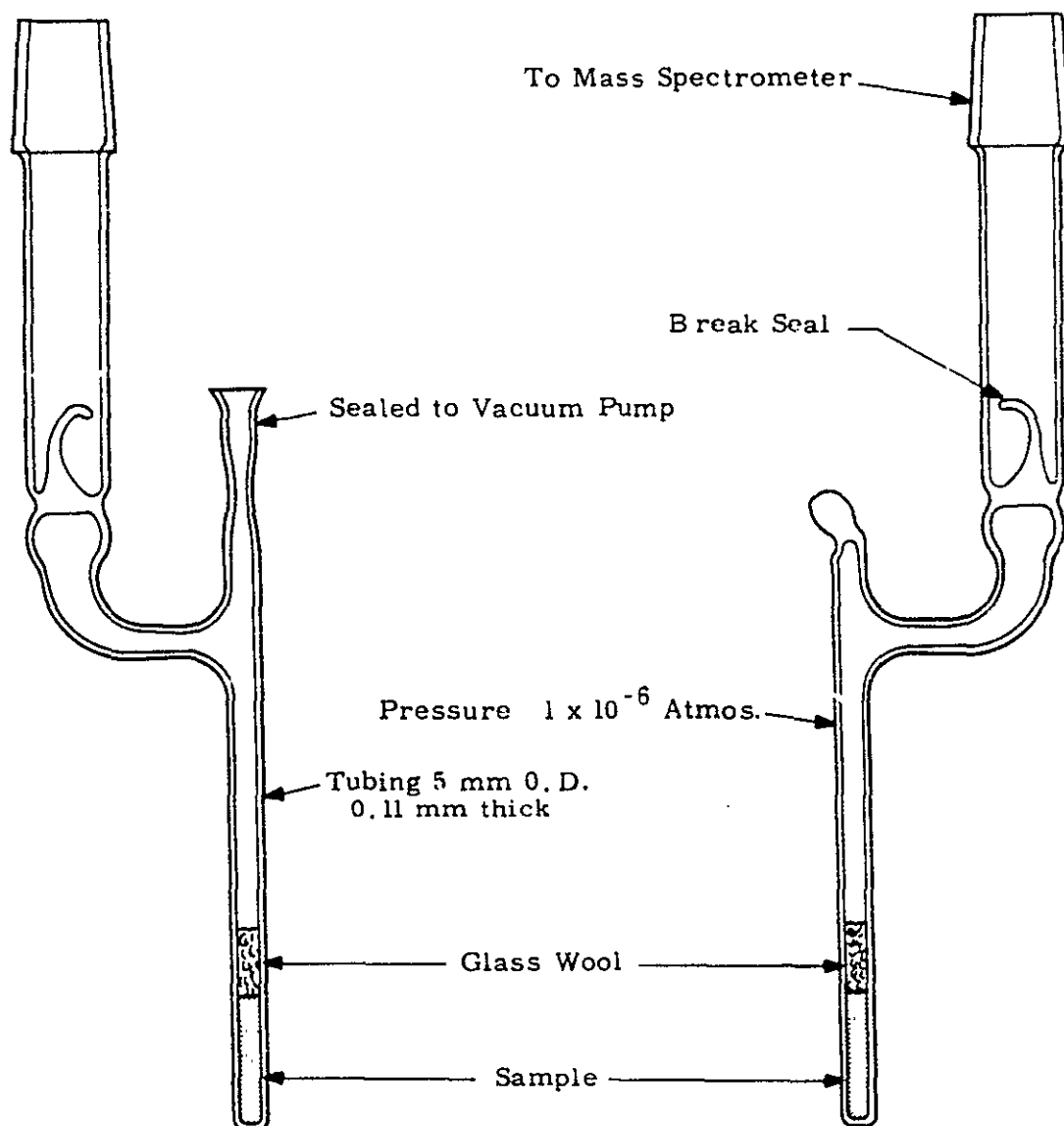
Four millimoles of cesium was used in each experiment, corresponding to 1.1 gm $Cs_2ZnFe(CN)_6$ and equivalent to 0.68 gm CsCl. When cesium chloride was the final product, iron, zinc, and nickel were analyzed spectrographically. Radiocesium was determined by a gamma well scintillation counter. All chemicals used in this investigation were reagent grade, and the anion exchange resin was Dowex-1, X4, 50-100 mesh. The X-ray analysis was done on a North American Philips X-ray diffractometer. The gases produced during the radiation experiments were analyzed on a modified Consolidated-Nier mass spectrometer, Model 21-201. The glass vessels used to contain the material to be irradiated by the Van de Graaff accelerator were made of 5 mm outside diameter pyrex tubing with a 1 mm wall thickness. The tube was sealed to a pryex system readily adapted to the mass spectrometer as shown in Figure 1. When using the cobalt-60 source, a 1 inch outside diameter vessel with a twenty-four millimeter volume capacity was used. A cerric sulfate dosimeter was used to determine the dosage rate of 1.9 Mev electrons produced by the Van de Graaff accelerator. The G value (molecules of cerric ion reduced per 100 electron volts) was 3.5 molecules/100 ev. This was determined with a known cobalt-60 source as a primary standard.

IV. DATA AND RESULTS

A. Composition and Crystal Structure

A sample of cesium zinc ferrocyanide was prepared in the laboratory from reagent grade cesium and zinc nitrates and potassium ferrocyanide, washed thoroughly, dried at 100 C for four hours, and analyzed chemically for cesium, zinc, iron, and water. The results obtained are compared with the theoretical values for $Cs_2ZnFe(CN)_6 \cdot H_2O$ in Table I.

To Mass Spectrometer

B reak Seal

Sealed to Vacuum Pump

Pressure 1×10^{-6} Atmos.

Tubing 5 mm O. D.
0. 11 mm thick

Glass Wool

Sample

RADIATION VIALS

FIGURE 1

TABLE I

CESIUM ZINC FERROCYANIDE ANALYSIS

	Composition, Weight Per Cent	
Element	Experimental	Theoretical ($Cs_2 ZnFe(CN)_6 \cdot H_2O$)
Cs	45.0	47.4
Zn	10.4	11.6
Fe	10.4	10.0
H_2O	4	3.2

Additional experiments were conducted using a thermal balance to further elucidate the degree of hydration and thermal stability of cesium zinc ferrocyanide. Two samples of cesium zinc ferrocyanide were prepared as before and washed thoroughly, but different drying techniques were used. One sample was dried at 25 C in dry air. The other sample was air dried at 100 C for four hours. The former procedure produced a yellow-green solid; the latter procedure produced a Prussian blue material, the color of which may be due to the presence of a trace amount of ferric ferrocyanide formed by thermal decomposition. Fresh'y prepared undried cesium zinc ferrocyanide is white to light yellow in appearance. The two samples were placed in procelain boats and weighed on the thermal balance. The weight loss was determined as a function of temperature, the rate of increase in temperature being maintained constant. The results of typical experiments are shown in Figure 2, and indicate approximate di-hydrate and mono-hydrate compositions for the 25 C air dried and the 100 C oven dried samples, respectively. Thus on this basis the calculated formula weight of the "di-hydrate" material was found to be 586, a factor of only 1.012 higher than the theoretical formula weight corresponding to $Cs_2 ZnFe(CN)_6 \cdot 2H_2O$. Similarly, the calculated formula weight of the "mono-hydrate" material was 563, a factor of 1.0036 higher than the theoretical formula weight of $Cs_2 ZnFe(CN)_6 \cdot H_2O$. Abrupt decreases in weight as shown in Figure 2
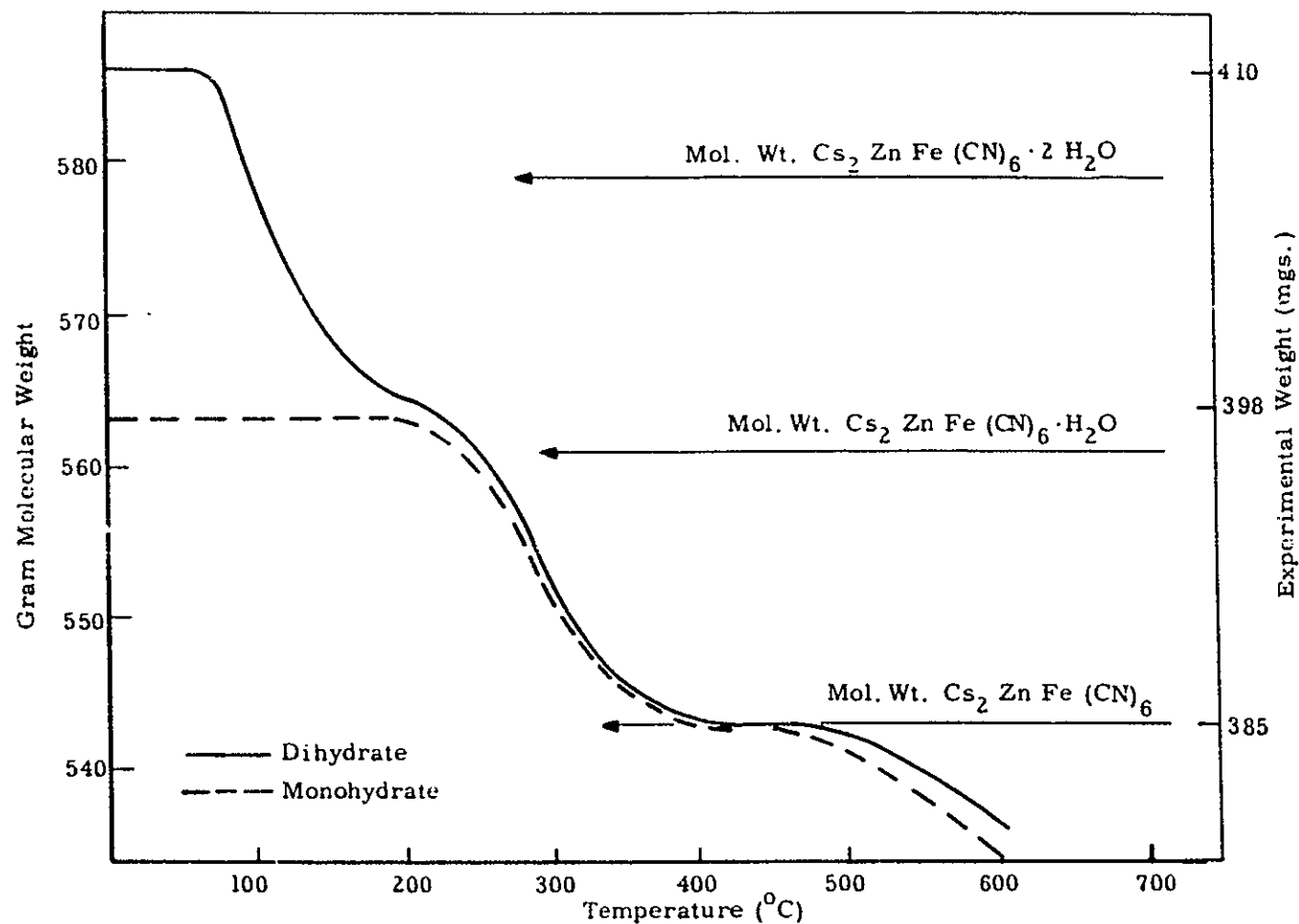
THERMAL BALANCE STUDIES OF CESIUM ZINC FERROCYANIDE DECOMPOSITION
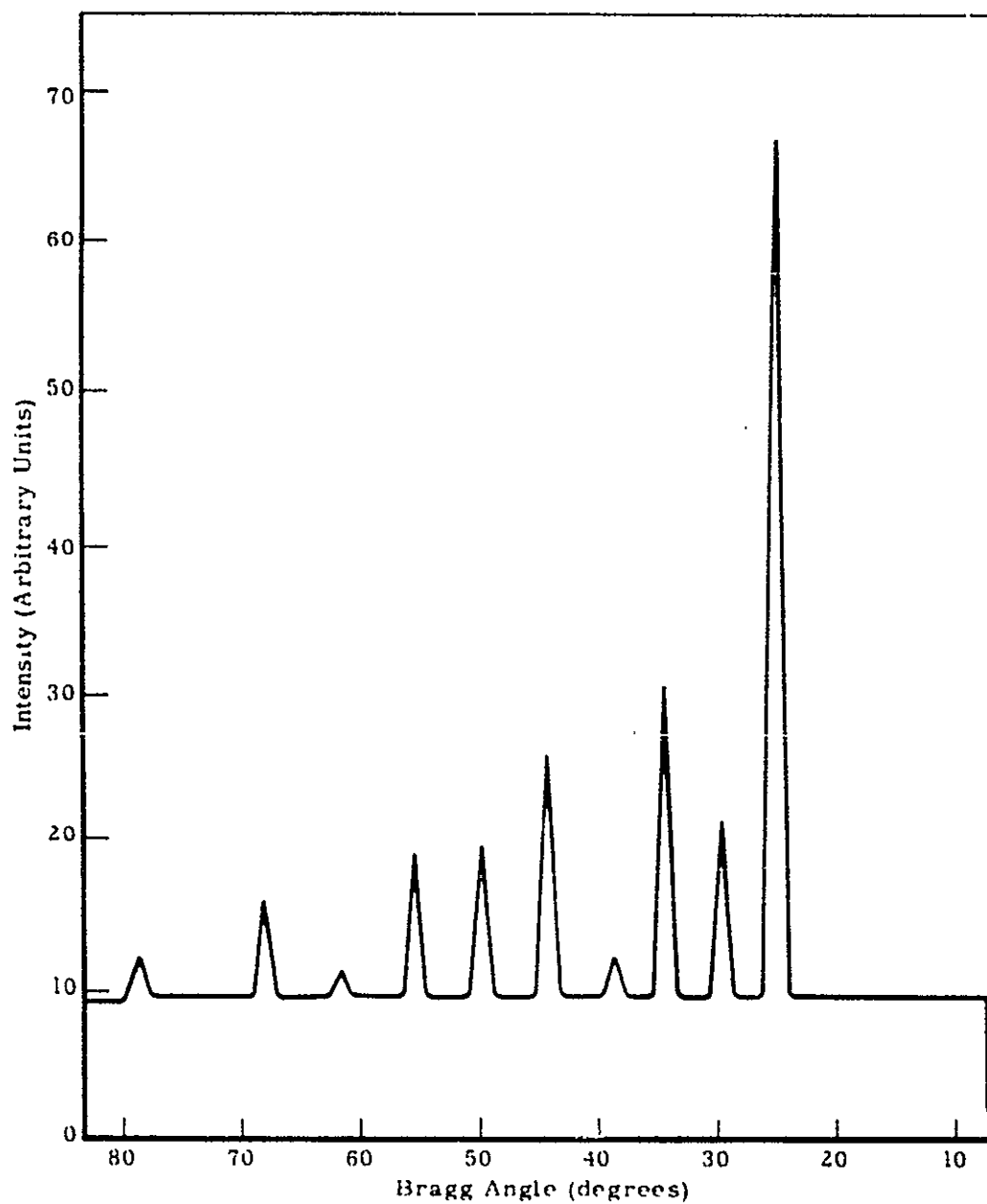
FIGURE 2

at 85 C and 190 C indicate the temperatures at which the first and second molecules of water started to evolve, respectively. On further heating, the compound itself started to decompose at about 480 C.

Powder X-ray diffraction studies were also made. Analysis of the sharp detailed patterns obtained, using copper-$K\alpha$ radiation, (Figure 3) indicated that cesium zinc ferrocyanide is isomorphous with potassium zinc ferrocyanide, $K_2ZnFe(CN)_6$.[9] The crystal is face centered cubic with a cell parameter of 10.2 Å versus 9.98 Å for the potassium compound. The calculated crystallographic density is about 3.44 grams/cc. The unit cell is shown in Figure 4.

## B. Radiation Stability of Cesium Zinc Ferrocyanide

The first experiment was made with the Chemical Research cobalt-60 source to determine the radiation stability of cesium zinc ferrocyanide. Finding the dosage rate to be too small for meaningful results, a Van de Graaff electrostatic accelerator belonging to the Calibrations Operation of the Hanford Laboratories was used for the rest of the experiments. The energy of the electrons produced by the Van de Graaff accelerator was 1.9 Mev. The gases produced were analyzed with a mass spectrometer.

Samples for Van de Graaff irradiation were sealed in glass vials and evacuated to a pressure of about 10^{-6} mm mercury. A plug of glass wool inserted in the vials prevented escape of the sample. The dosage rates of the electrons emitted from the Van de Graaff accelerator were calibrated by determining the extent of reduction of a ceric sulfate dosimeter. A ferrous sulfate dosimeter was used with the cobalt-60 source. It should be noted that the ceric sulfate dosimeters used were exposed to a dosage rate higher by a factor of about a thousand than in previous work done by other workers. However, the change in dosage rate as indicated by the ceric sulfate dosimeter compared to the change in the current of the Van de Graaff accelerator indicates that the linearity still holds for this dosimeter at these high dosage rates. Some of the sample vials were evacuated at room temperature, and others were heated at 200 C with an oil bath while being evacuated for more

X-RAY POWDER DIFFRACTION PATTERN CESIUM
ZINC FERROCYANIDE

FIGURE 3

Cs_2 Zn $Fe(CN)_6$

MOLECULAR wt. = 547, 49 wt. % Cs

CESIUM ZINC FERROCYANIDE

UNIT CELL

FIGURE 4
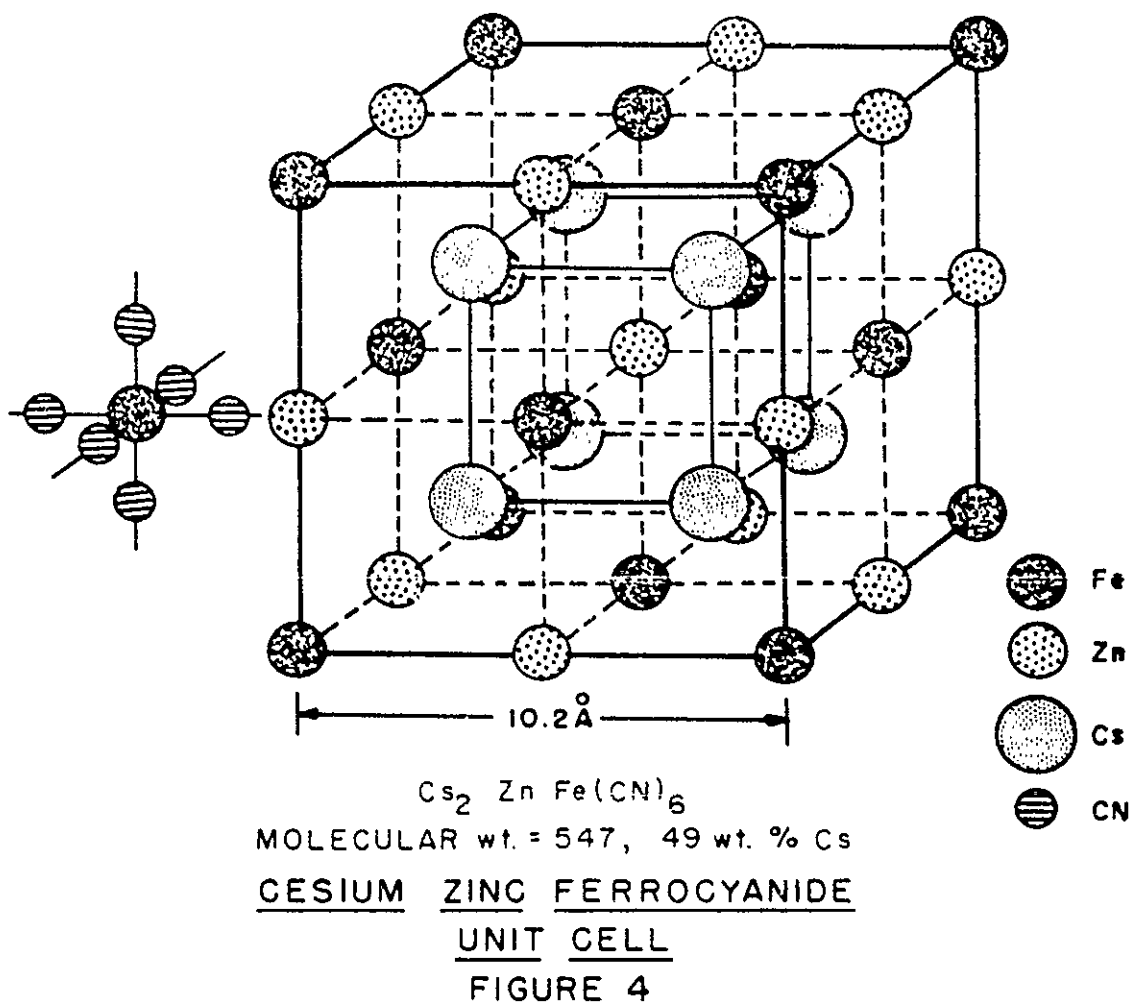
efficient out-gassing. One vial containing cesium chloride was dried thoroughly at 450 C in air and then out-gassed at 200 C.

Table II summarizes the results obtained for cesium zinc ferrocyanide mono-hydrate and for anhydrous cesium zinc ferrocyanide as well as for several other materials of interest. The G_g values for the different cesium zinc ferrocyanide compounds are calculated as molecules of gases produced per 100 electron volts absorbed. It will be noted that approximately the same value for G_g was obtained for the mono-hydrate with cobalt-60 gammas as with the Van de Graaff despite the different types of radiation and the widely different dose rates. G_g for anhydrous cesium zinc ferrocyanide is much smaller, but still not negligible.

Traces of water in the compounds used and gases absorbed in the glass vials[10] are believed to have caused large uncertainties in the results. It appears, however, that some decomposition occurs when either of the cesium zinc ferrocyanide compounds are exposed to radiation, and that pressure will build up in sealed vessels containing cesium zinc ferrocyanide. Thus a spherical five thousand curie cesium-137 source should produce a maximum radiation dosage at the center of about 2×10^7 rads/hr (a sphere is the worst possible case from the standpoint of self absorption of radiation). This source would have a diameter of about 8.65 centimeters if loose packed (pack density = 0.9 gms/cc) and would have a free volume of about 250 cubic centimeters. Pressures of 119 atmospheres and 12.5 atmospheres would build up inside the sphere after six months for the mono-hydrate and anhydrous cesium zinc ferrocyanide, respectively. These numbers are based on the assumptions that the G_g values remain constant over this period of time and that change in free volume due to decomposition is negligible. This problem might be overcome by building a source container that will either stand the pressure or permit the gases produced to escape, or by converting the ferrocyanide compound to a radiation stable compound such as cesium chloride.

TABLE I

RADIATION STABILITY STUDIES

SOURCE: 1.9 Mev Electrons from Van de Graaff Accelerator (except where noted)

Sample	Weight (gms)	Heat Treat	Dose Rate (Rads/hr)	Dose (Rads)	Gases, mole per cent						Pressure (mm) 25° C	G_g*
					CO_2	N_2	CO	CH_4	H_2	H_2O		
$Cs_2ZnFe(CN)_6 \cdot H_2O$**	7.3656	25° C	4.7×10^5	1.13×10^7	-	-	-	-	-	-	11	0.0457
$Cs_2ZnFe(CN)_6 \cdot H_2O$	0.343	25° C	1.53×10^8	1.5×10^8	36	2	-	-	36	26	29	0.067
$Cs_2ZnFe(CN)_6 \cdot H_2O$	0.440	25° C	1.53×10^8	1.58×10^9	31	26	-	2	22	19	448	0.076
$Cs_2ZnFe(CN)_6$	0.426	200° C	1.53×10^8	1.58×10^9	1	75	-	9	15	-	17	0.003
$Cs_2ZnFe(CN)_6$	0.158	200° C	2.3×10^9	2.3×10^{10}	1	68	-	7	24	-	230	0.008
CsCl	0.476	25° C	2.25×10^9	1.9×10^{10}	--	6	30	1	43	20	85.8	-
CsCl	0.510	450° C***	2.3×10^9	2.3×10^{10}	-	2	23	-	25	-	12.5	-
$2CsCl \cdot ZnCl_2$	0.609	25° C	2.2×10^9	2.2×10^{10}	5	17	21	2	54	1	390	-
$2CsCl \cdot ZnCl_2 + 1/2Fe_2O_3$	0.208	200° C	2.3×10^9	2.3×10^{10}	79	2	9	-	10	-	28	-
Glass Wool ****	-	200° C	2.2×10^9	2.2×10^{10}	48	-	52	-	-	-	57	-

* G_g = number of molecules of gases produced per 100 ev absorbed.

** Cobalt-60 Source: dosage in roentgens, (gas analysis not made).

*** Preheat to 450° C and then out-gassed at 200° C.

**** Blank with same amount of glass wool used in other sample vials.

-18-

HW-48832

C. Calcination-Chlorination Packaging Process

It was thought that a mixture of radiation stable non-hygroscopic compounds could be prepared from cesium zinc ferrocyanide by selective chlorination. From thermodynamic considerations, exposure to a suitable mixture of chlorine and oxygen (air) should convert cesium zinc ferrocyanide to a mixture of cesium chloride, zinc oxide, and ferric oxide - all stable non-hygroscopic materials. Experiments were, therefore, carried out as described under Experimental. It was found under the conditions used and with a variety of gas mixtures and temperatures, however, that zinc oxide was not formed but rather a mixture of the chlorides of cesium and zinc with ferric oxide. X-ray powder diffraction studies showed that the zinc and cesium were associated together as the addition compound $2CsCl \cdot ZnCl_2$. This non-hygroscopic material can also be precipitated by mixing aqueous solutions of the cesium and zinc chlorides,[11] and its stability may well account for the fact that the thermodynamic expectations were not realized. The $2CsCl \cdot ZnCl_2 \cdot 1/2Fe_2O_3$ material is also non-hygroscopic, however, and is apparently entirely suitable as a source material.

It was found during the experiments that cesium volatilized if the chlorine partial pressure during the process was too low. This volatilization was prevented, however, when the chlorine pressure was increased to 0.5 atmospheres. The lowest temperature for conversion of the ferrocyanide was 350 C, and the time required at this temperature was two hours. An additional three hours after the chlorine gas was shut off was needed to convert all of the iron to its oxide. Even under these conditions a trace of a white material evolved and collected on the cooler portions of the equipment. This at first was thought to be cesium oxide but later experiments with cesium-137 tracer showed that less than 0.01 per cent was lost due to evaporation. The bulk of the white deposit is probably an ammonium compound formed by reaction of ferrocyanide and water.[12]

The calcination-chlorination product is a rust colored, granular, easily packed material. An empirical tap density was found by placing a weighed amount in a small graduated tube and tapping the tube against a solid surface until the volume of the material remained constant. This density was 0.9 gm/cc. A packed density, determined by compressing a sample under a pressure of 100,000 psi at room temperature, was found to be 4.0 gms/cc. The radiation stability of this product (see Table III) coupled with its chemical stability and high specific activity may make it a very desirable cesium source material. A comparison of specific activities for this and several other cesium products is shown in Table III, and a flowsheet for this operation is shown in Figure 5.

TABLE III

SPECIFIC ACTIVITIES OF CESIUM PRODUCTS

Product	Mol. Wt.	Cs^{137} c ries/gm	Density (gm/cc)	Cs^{137} curies/cc
Cs	135[1]	35	1.9	66.5
CsCl	171	27	3.97 (2.7-3.1)[2]	110 (71-77)
$Cs_2ZnFe(CN)_6$	547	17	3.44	59.5
$2CsCl \cdot ZnCl_2 + 1/2\ Fe_2O_3$	557	17	0.9[3] 4.0[4]	15.3 68

1. Average for fission product cesium.
2. Experimental products (Oak Ridge).
3. Tap density.
4. Pressed to 100,000 psi (room temperature).

D. Calcination - Leaching Packaging Process

It was thought that a simple calcination of cesium zinc ferrocyanide would convert all of the metals to their oxides and that a water leaching might then separate cesium from the more refractory oxides. Therefore, a

$$Cs_2 \, Zn \, Fe \, (CN)_6$$

Dry

Pulverize

Chlorine 0.5 Atm.
Air   0.5 Atm.

Calcine
$350^{\circ}C$
2 hrs.

Gaseous
Waste

Air   1 Atm.

Calcine
$350^{\circ}C$
2 hrs.

Gaseous
Waste

$$2 \, Cs \, Cl \cdot Zn \, Cl_2 \; + \; 1/2 \, Fe_2 \, O_3$$
$$(\sim 17 \; curies/gm)$$
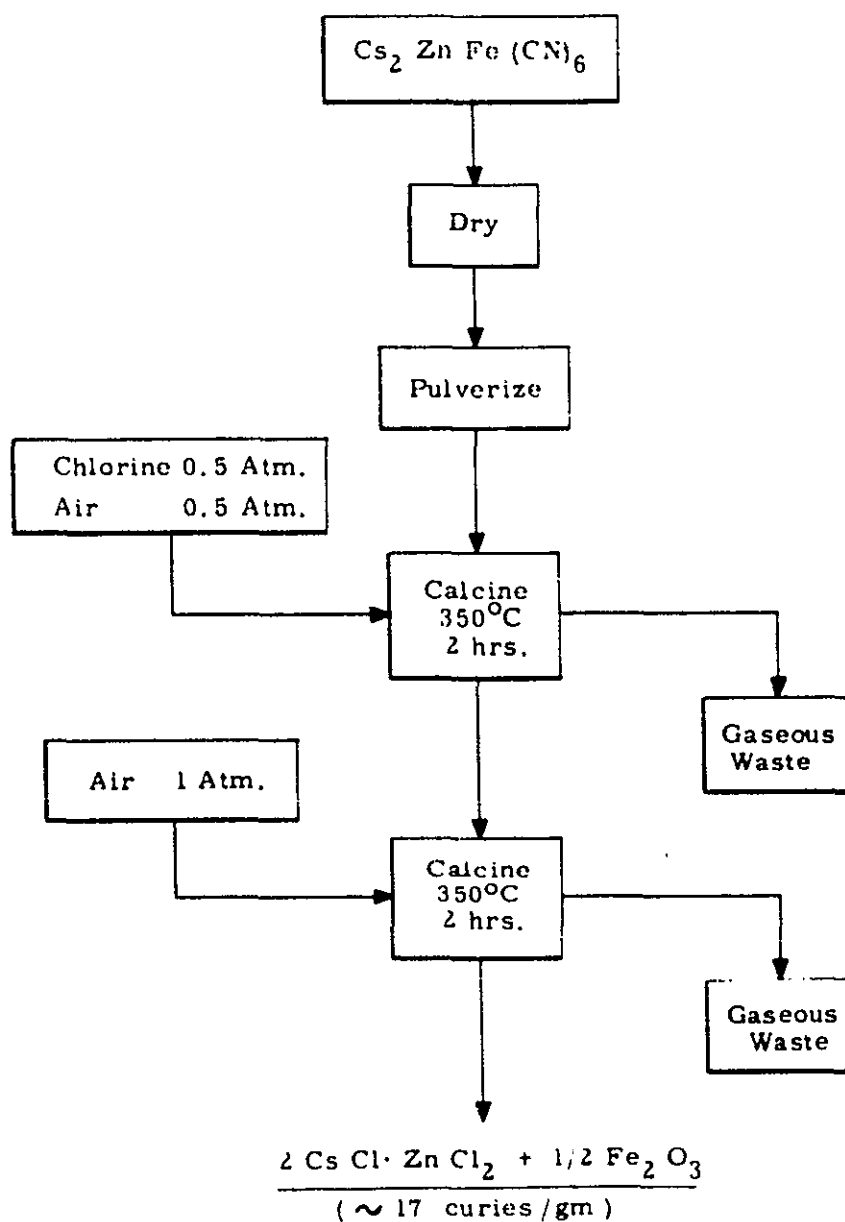
CALCINATION - CHLORINATION FLOWSHEET

FIGURE 5

series of calcinations were attempted at different temperatures, both with
air and oxygen, to determine the effect of these variables on extent of
recovery and product purity.   Table IV summarizes the results.   Notice
that a temperature of 700 C or greater causes loss of cesium through
evaporation.   If pure oxygen is used, the calcination temperature can be
reduced and still obtain good recovery cesium by the leaching process.   It
was found that a pure cesium chloride sample could be prepared in a tempera-
ture range of 550 C to 600 C for four hours with a radiochemical recovery
of 99 per cent or greater.   The weight of the purified cesium chloride obtained
by this method also was that expected.   Spectroscopic analysis showed the
final product to contain less than 0. 1 per cent zinc and iron.   The flowsheet
for the calcination - leaching process for the conversion of cesium zinc
ferrocyanide to cesium chloride is shown in Figure 6.

TABLE IV

CALCINATION OF CESIUM ZINC FERROCYANIDE

Oxygen Content (Per Cent)	Temp. ° C	Cesium Leached (Per Cent)	Cesium Evap. (Per Cent)
20 (Air)	350	45	not detected
20 (Air)	450	65	not detected
20 (Air)	550	99. 9	not detected
20 (Air)	600	99. 9	not detected
20 (Air)	700	95	5
100	450	95	not detected

During some of the calcination experiements, pryophoric reactions or
mild explosions were observed.   However, two water washes were sufficient
to remove the residual nitrate, which presumably caused the explosions.
Washing with water did lead to some peptization of the precipitate.   However,
it was possible to prevent this by the use of 0. 01 $\underline{M}$ hydrochloric acid.
Ammonium chloride, ammonium sulfate, or ammonium phosphate might also
be satisfactory wash media.   No further trouble was experienced.

$Cs_2 Zn Fe (CN)_6$
100 gms. Dry Weight Basis
49 gms. Cs, Slurry Vol. $\sim$ 300 ml

↓

Dry

↓

Pulverize

↓

Air → Calcine
(4 hrs., 550°C) → Gaseous Waste

Water
500 ml

↓

Leach → ZnO, $Fe_2 O_3$
Waste, 85 gms.

↓

Evaporate

Hydrochloric Acid
50 ml 12 $\underline{M}$ →

↓

Heat 450°C

↓

Cs Cl $\begin{cases} 99\% \text{ Cs Cl} \\ < 0.1\% \text{ Fe, Zn} \\ \sim 27 \text{ Curies/gm} \end{cases}$
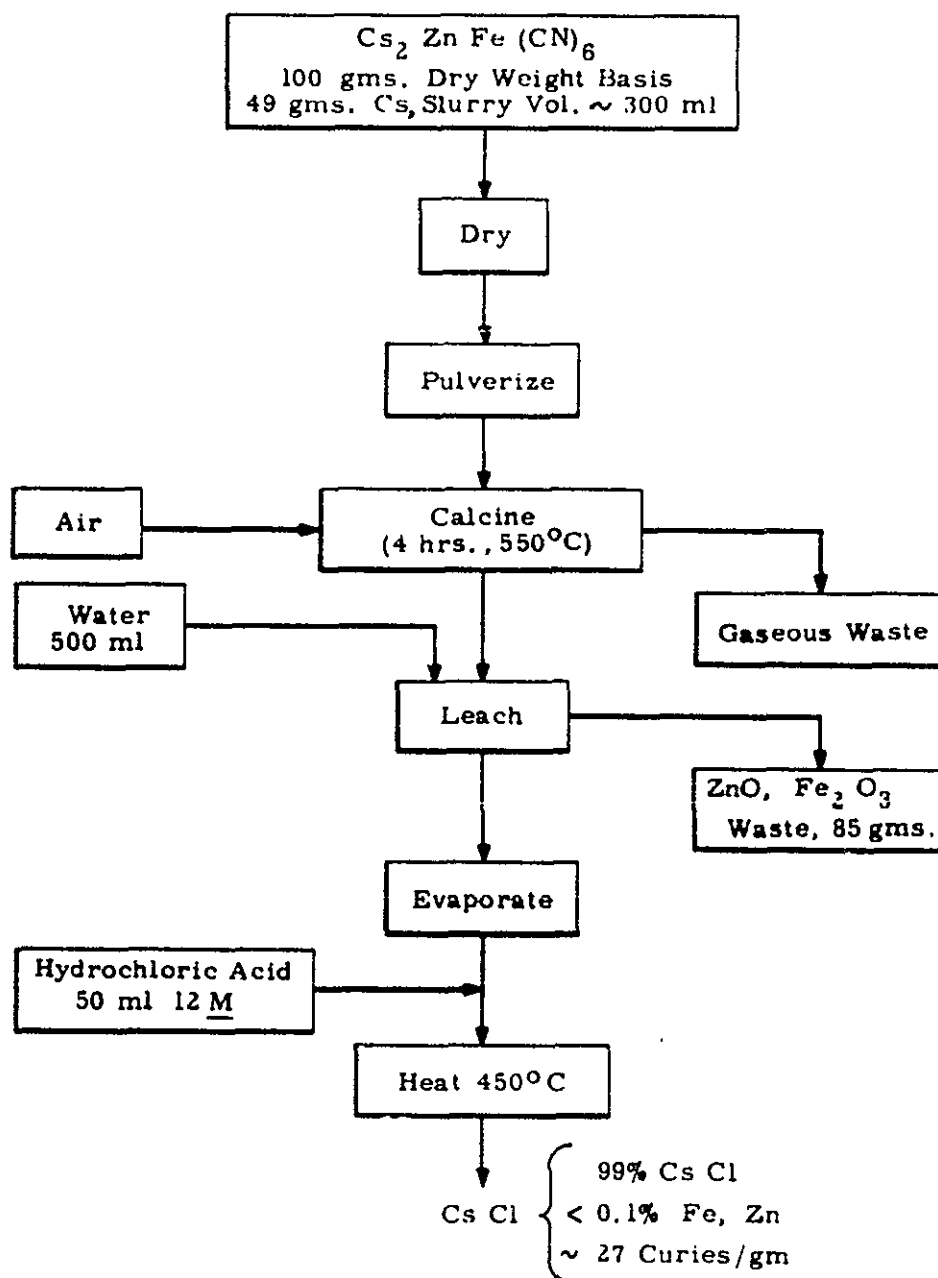
CALCINATION - LEACHING FLOWSHEET

FIGURE 6

E. Wet Chemical Packaging Process

1. Dissolution of Cesium Zinc Ferrocyanide

Because of its high stability and low solubility, cesium zinc ferro-
cyanide is exceedingly difficult to dissolve. Only three of the reagents tried,
aqua regia, sulfuric acid, and phosphoric acid dissolved the cesium compound,
and then only at elevated temperatures. Table V lists the various reagents
tried and the results. One and one-half times as much phosphoric acid and
aqua regia was needed for complete dissolution as was required with sulfuric
acid, so sulfuric acid was used as a basis for subsequent development.
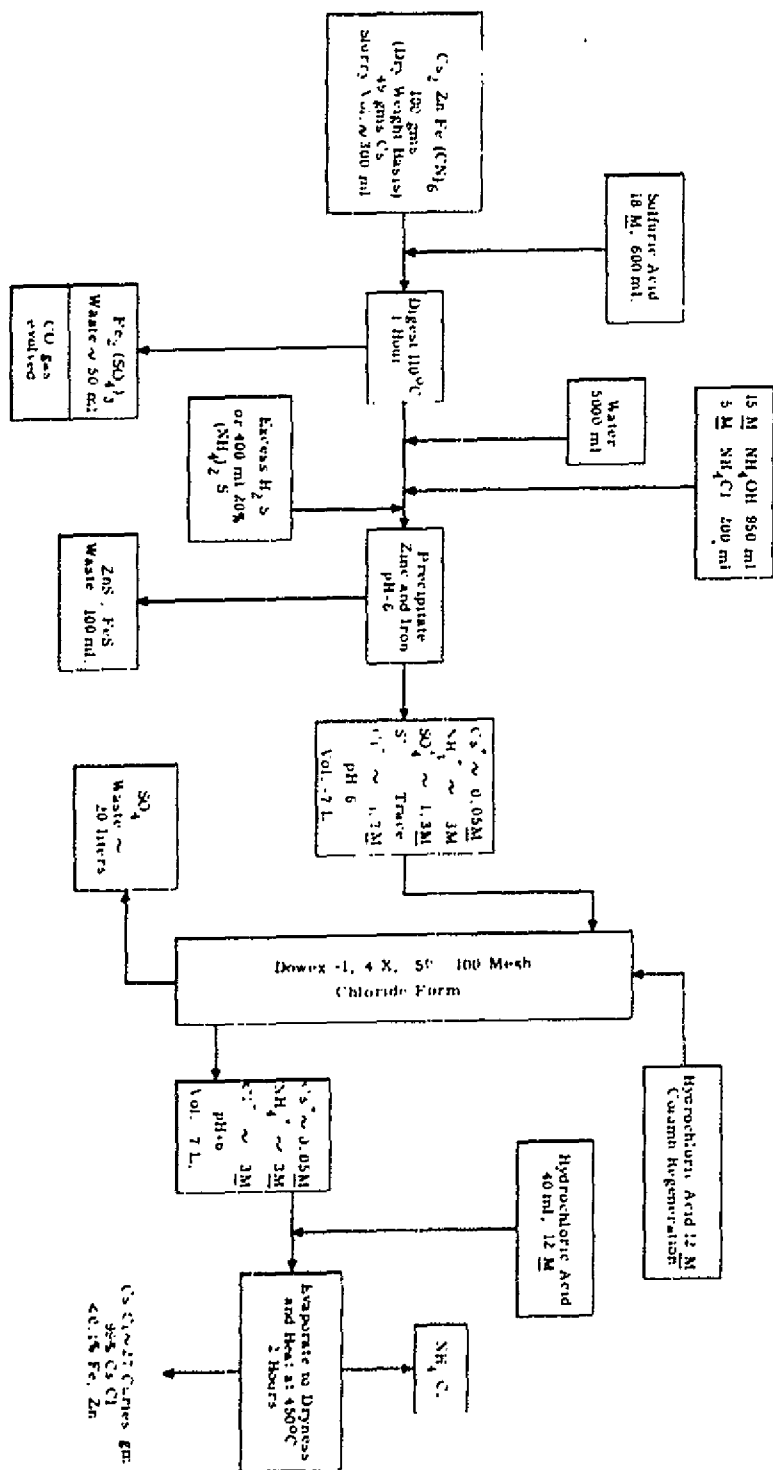Sulfuric acid will dissolve either freshly precipitated or dried cesium zinc
ferrocyanide.

TABLE V

DISSOLUTION OF CESIUM ZINC FERROCYANIDE

Reagent	Conc. M	Temp. ° C	Change in Physical Appearance	Cesium Recovery Per Cent
Nitric Acid	15	25	Yellow ppt.	10
Nitric Acid	Fuming	25	Yellow ppt.	10
Hydrochloric Acid	12.4	25	Green ppt.	15
Acetic Acid	17.5	25	No change	1
Acetic-Hydrochloric	8-6	25	Green ppt.	5
Perchloric Acid	11.7	25	Brown ppt.	5
Sulfuric Acid	18	25	Yellow-Green ppt.	30
Sulfuric Acid	18	110	Yellow soln. + ppt.	100
Aqua Regia	- -	25	Black	25
Aqua Regia	- -	110	Clear soln.	100
Phosphoric Acid	14.6	25	Partly dissolved	25
Phosphoric Acid	14.6	110	Clear Soln.	100
Hydrofluoric Acid	27.6	25	Green ppt.	5
Sodium Hydroxide	10	25	None	1
Ammonium Hydroxide	15	25	None	1
Sodium Dichromate	2	25	Orange ppt.	1

2. Purification from Extraneous Ions

In the wet chemical process developed for recovering cesium from cesium zinc ferrocyanide, the compound is dissolved in hot sulfuric acid and allowed to digest for one hour to insure a complete removal of any cyanide left after dissolution. The solution is separated from the ferric sulfate formed, which is largely insoluble in sulfuric acid. The zinc and residual iron are then removed by a sulfide precipitation after buffering to about a pH of 6 with ammonia and ammonium chloride. The solution is passed through a Dowex-1 anion exchange resin in the hydroxide or chloride form (the chloride form is regenerated much more readily) to remove the sulfate and sulfide ions. The flow rate used was 3 $ml/cm^2/min$, but faster rates may well be equally effective. Sulfate was not detected in the effluent using barium nitrate as a qualitative test. It might be noted that the Oak Ridge National Laboratory developed the ion exchange process for sulfate removal and has used it successfully in conjunction with the Alum process to obtain kilocurie sources of cesium-137. The eluate is boiled to dryness to drive off ammonia, acidified with hydrochloric acid, and again evaporated to dryness. Heating to a temperature of about 450 C was found necessary to remove all trace of water. Radiation stability experiments have indicated pressure build-ups with cesium chloride less rigorously dried. Oak Ridge, too, has found it necessary to heat their final product to about this temperature. The final product contained less than 0.1 per cent zinc and iron, as shown by emission spectra. Figure 7 demonstrates the process. Radiochemical and gravimetric recovery of cesium was 99 per cent.

Purex Plant 1WW first cycle waste solution was spiked into a cesium zinc ferrocyanide precipitate and the activities followed in a demonstration run. Table VI outlines the decontamination from cesium of other radioisotopes in this process. Since the ferrocyanide precipitation and previous steps in the cesium zinc ferrocyanide process[6] decontaminate cesium rather well from the other fission products, the final product should be of very high radiochemical purity.

WET CHEMICAL FLOWSHEET

FIGURE 7

Cs, Zn Fe (CN)$_6$ 181 gms (Dry Weight Basis) +9 gms Cs Slurry Vol ~300 ml

Sulfuric Acid 18 M, 600 ml

Digest 110°C 1 Hour

Fe$_2$ (SO$_4$)$_3$ Waste ~50 ml / CO gas evolved

Water 5000 ml

15 N NH$_4$OH 950 ml / 5 M NH$_4$Cl 200 ml

Excess H$_2$S or 400 ml 20% (NH$_4$)$_2$ S

Precipitate Zinc and Iron pH-6

ZnS, FeS Waste 100 ml

Cs ~ 0.05M / NH$_4$ ~ 3M / SO$_4$ ~ 1.5M / S ~ 1.5M / Cl Trace / Vol 7 L / pH 6

SO$_4$ Waste ~ 20 liters

Dowex -1, 4 X, 50-100 Mesh Chloride Form

Hydrochloric Acid 12 N Column Regeneration

Cs ~ 0.05M / NH$_4$ ~ 3M / Cl ~ 3M / Vol 7 L / pH-0

Hydrochloric Acid 40 ml, 12 M

Evaporate to Dryness and Heat at 450°C 2 Hours

NH$_4$Cl

Cs Cs-137 Cures gm >9% Cs Cl <0.1% Fe, Zn

TABLE VI

REMOVAL OF FISSION PRODUCTS FROM CESIUM IN THE WET CHEMICAL PROCESS

Radioisotope	Initial Activity	Decontamination Factor*			
		$SO_4^=$ Precipitation	$S^=$ Precipitation	Ion Exchange	Total
Zr-Nb-95	1.78×10^9 γ/m	2	3.8	20	160
Ru-Rh-106	2.0×10^8 γ/m	1	2.5	7	17.5
Ce-Pr-144	$3.5 \times 10^8 \gamma/m$	8.8	1	1	8.8
Sr-Y-90	$2.0 \times 10^7 d/m (\beta)$	5	1	1	5
Pu-239	5.2×10^6 $d/m (\alpha)$	10.8	**	> 1000	>1000

* Initial activity divided by the final activity.

** Lost Sample

F. Electrochemical Packaging Process

In order to eliminate steps involving sulfide precipitation and ion exchange methods, an electrolytic process was developed. After the cesium compound was dissolved in sulfuric acid and the insoluble ferric sulfate removed, the remaining sulfate was precipitated with a slight excess of lead nitrate, contrifuged, and the supernate placed in a water jacketed mercury - cathode cell, as shown in Figure 7. A voltage of 12 volts was impressed across the electrodes and gave a current density of 0.3 amperes/cm^2 with the particular cell used. The iron, lead, and zinc were reduced at the mercury cathode within 30 minutes; the solution containing cesium nitrate was then removed and boiled down to dryness with hydrochloric acid. A cesium chloride sample prepared in this manner contained less than 0.1 per cent iron, lead, and zinc. A gravimetric cesium yield of 99 per cent was realized coupled with greater than 99 per cent recovery of the radiocesium.

The alkaline metals and zirconium-niobium were found not to reduce under these conditions. Ruthenium was also only partially removed by the electrolysis. Therefore, there is very little decontamination from these elements. In order to optimize conditions, acid concentrations should be 5 $\underline{M}$ or less, the mercury surface area should be large, and the current density adjusted to 0.3 amps/cm^2. [13] It was found that the mercury can be cleaned by washing with a dilute nitric acid solution, or by a simple distillation. A flowsheet for this process is shown in Figure 8. The lead nitrate step might be eliminated in the process by the addition of a stoichimetric amount of barium nitrate to precipitate the sulfate ion.

G. Applications to Nickel Ferrocyanide, Iron(III) Ferrocyanide, and zinc Ferricyanide

The above processes for cesium packaging were also tried using nickel ferrocyanide, ferric ferrocyanide, and zinc ferricyanide. The ratio of cesium to nickel and iron was one to three and the ratio of cesium to zinc was one to seven. In every process, with the exception of the calcination-leaching process, a cesium chloride sample was recovered with a chemical yield and purity as good as with cesium zinc ferrocyanide. When attempting a calcination of either nickel and ferri ferrocyanide, spattering occurred and 90 per cent of the cesium was lost. Additional work would have to be done in this respect if these scavenging agents were used in a cesium recovery process and it was desired to employ a calcination-leaching process.

V. DISCUSSION

Before any firm conclusions can be made as to the type of process which is most nearly optimum, certain additional information should be acquired. One investigation stands out as very important. Prototype cesium-137 sources should be prepared in order to observe the actual pressure build-up when such compounds as cesium zinc ferrocyanide, cesium sulfate cesium phosphate, and cesium oxide are used as the radiation source material.
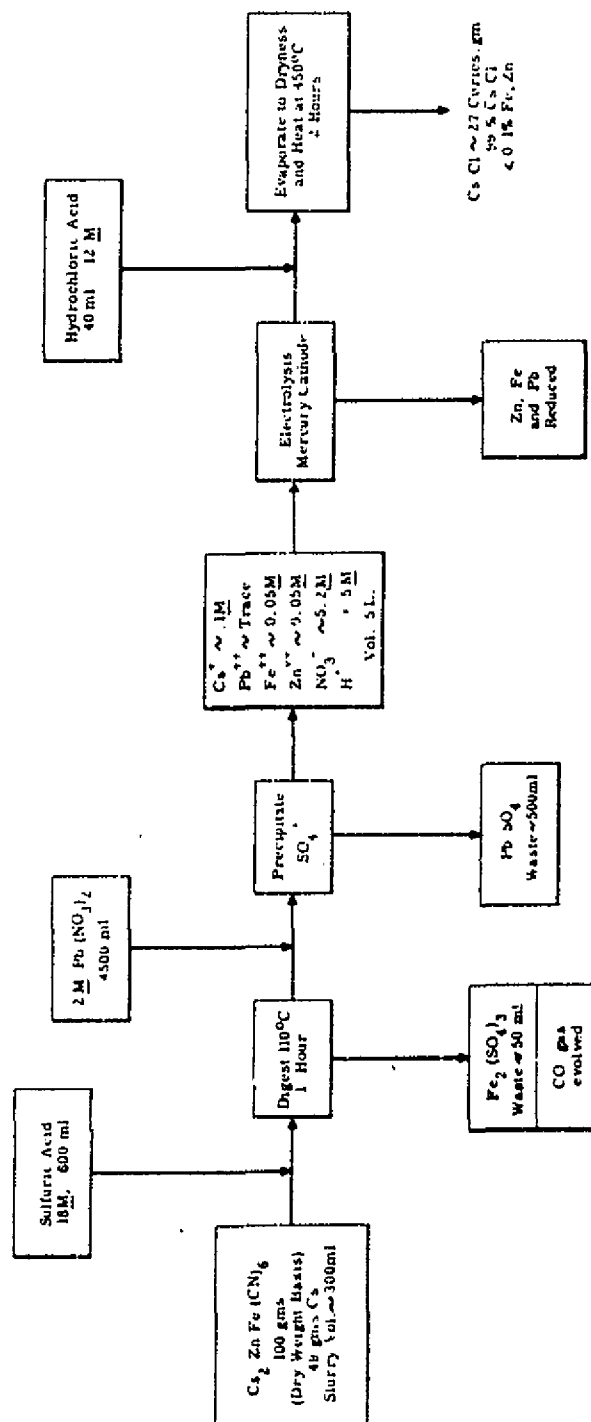
ELECTROLYTIC PROCESS

FIGURE 5

If any of these compounds are stable to self radiation, the process for packaging the cesium might be much simplified. Other information required for engineering development would include (1) handling characteristics of cesium zinc ferrocyanide (filtration and cetrifugation characteristics), (2) degree of washing required to prevent explosions in the calcination processes and washing techniques which would prevent peptization, (3) handling characteristics of iron sulfate and sulfide precipitates, (4) scale up factors and extent of radiation damage in the anion resin step in the wet chemical flowsheet, and (5) design and testing of a full size mercury cathode electrolysis cell.

All of the flowsheets presented were operable on a laboratory scale, and the choice between them for further development would be largely determined by engineering considerations. Each has certain advantages and disadvantages. Thus the calcination-chlorination process is compact and utilizes all "dry" chemistry but produces a product of somewhat less than ultimate specific activity, has an associated explosion hazard, and employs a corrosive gas. The calcination-leaching process has many of the advantages of the calcination-chlorination operation and produces a pure cesium chloride product, but requires higher temperatures and suffers the same pyrophoric reaction potential. It was also not applicable to all of the ferrocyanides and ferricyanides tested. In practice, the explosion difficulty can probably be controlled by either proper washing or by design of the calciner to safely contain the reaction. The wet chemistry processes eliminate the above hazard and produce a very pure product, but at the expense of somewhat bulkier equipment.

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